Supplementary Information

Mononuclear Sulfido-Tungsten(V) Complexes: Completing the Tp*MEXY (M = Mo, W; E = O, S) Series

Stephen Sproules,[*,†] *Aston A. Eagle,*[‡] *Graham N. George,*[‖] *Jonathan M. White,*[‡,¶] *and Charles G. Young*[§]

[†]WestCHEM, School of Chemistry, University of Glasgow, Glasgow G12 8QQ, United Kingdom, [‡]School of Chemistry, University of Melbourne, Parkville, Victoria 3010, Australia, [‖]Department of Geological Sciences, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5E2, Canada, [¶]Bio21 Molecular Science and Biotechnology Institute, University of Melbourne, Parkville, Victoria 3010, Australia, and [§]Department of Chemistry and Physics, La Trobe Institute for Molecular Science, La Trobe University, Melbourne, Victoria 3086, Australia

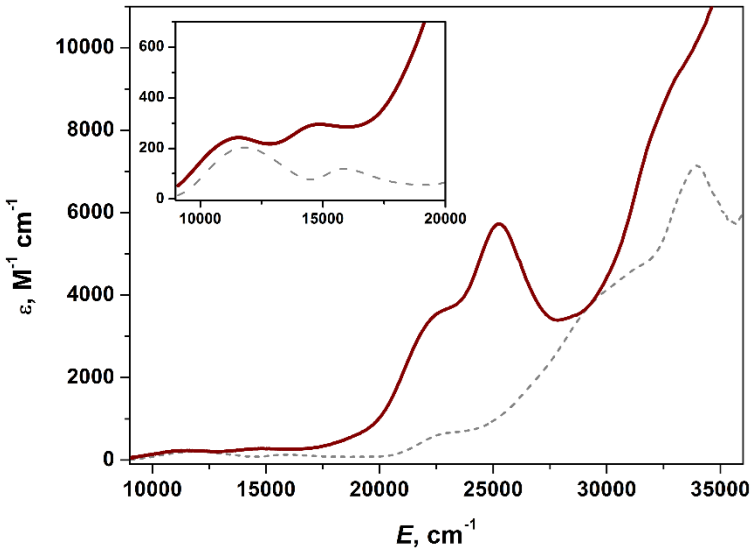

Figure S1. Electronic absorption spectrum of Tp*WS(tdt) recorded in dichloromethane solutions at ambient temperature. The dashed grey trace is the spectrum of Tp*WO(tdt). Inset shows an expansion of the low-energy region.

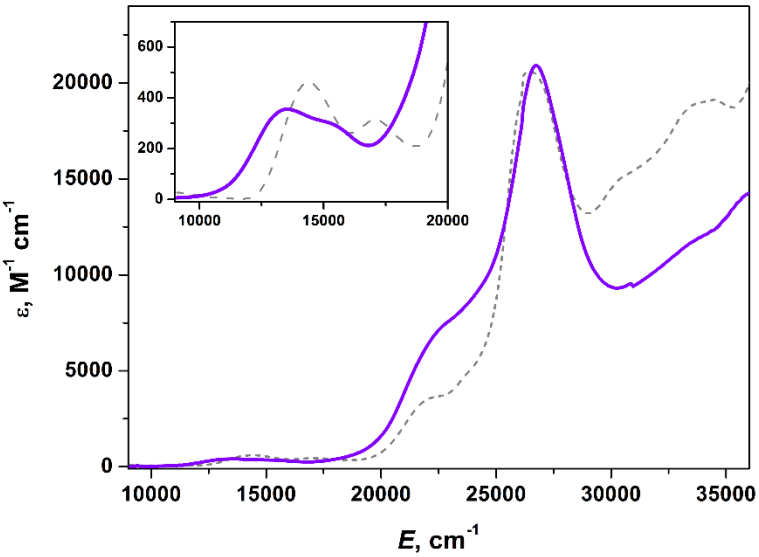

Figure S2. Electronic absorption spectrum of Tp*WS(qdt) recorded in dichloromethane solutions at ambient temperature. The dashed grey trace is the spectrum of Tp*WO(qdt). Inset shows an expansion of the low-energy region.

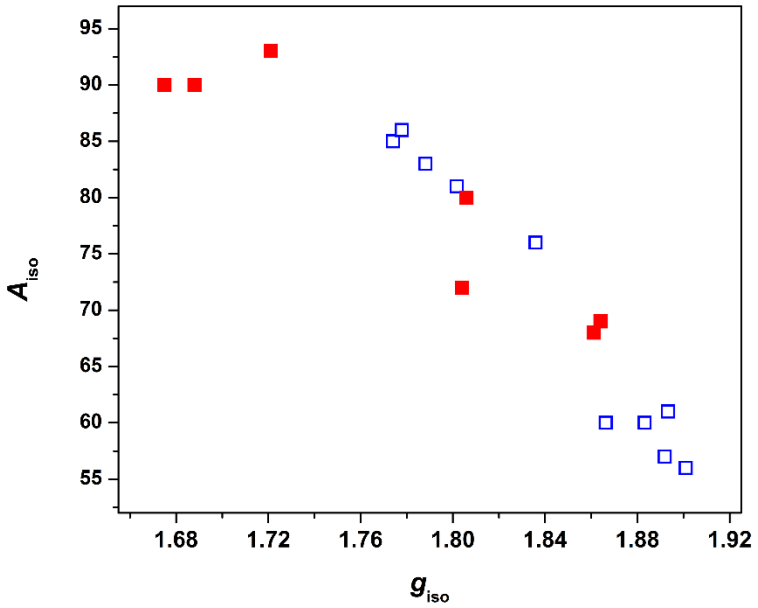

Figure S3. Correlation of the g_{iso} and A_{iso} values for Tp*WSXY (■) complexes overlaid with the Tp*WOXY (□) homologues.

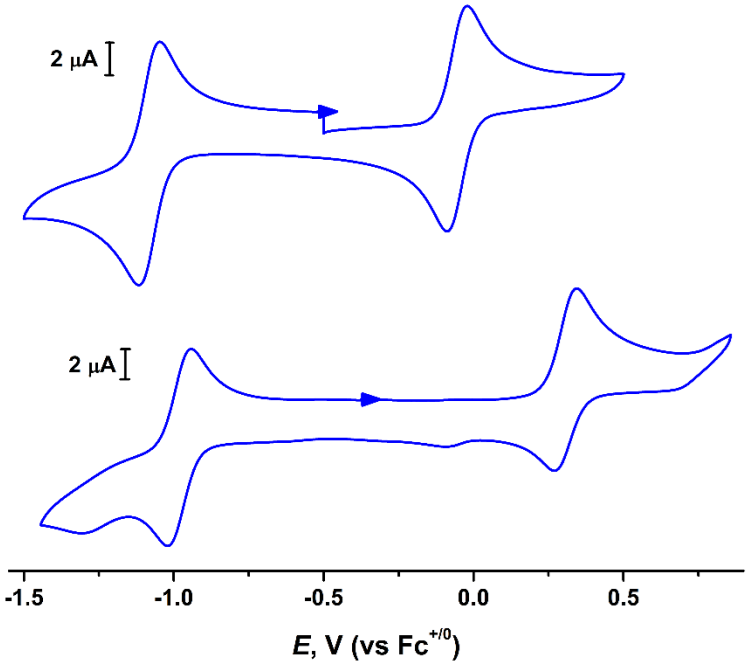

Figure S4. Cyclic voltammograms of Tp*WS(SPh)$_2$ (top) and Tp*WS(tdt) (bottom) recorded in CH_2Cl_2 solution containing 0.1 M [N(*n*-Bu)$_4$]PF_6 as the supporting electrolyte at a scan rate of 100 mV s^{-1}. Reduction potentials are referenced versus the $Fc^{+/0}$ couple. All Tp*WSXY with monodentate ligands exhibited a similar voltammogram to Tp*WS(SPh)$_2$; likewise TpWS(qdt) is similar to Tp*WS(tdt).

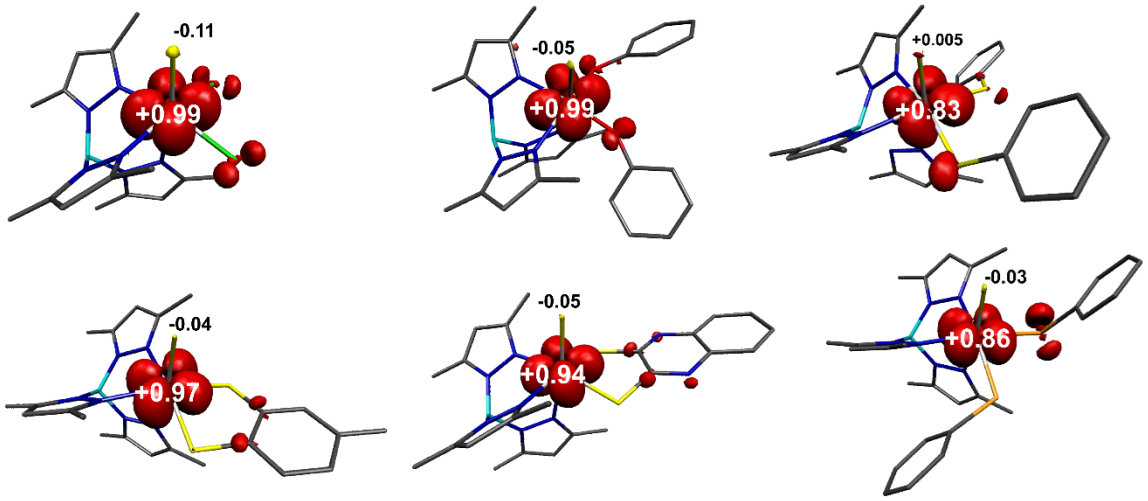

Figure S5. Mulliken spin density plots for Tp^*WSCl_2, $Tp^*WS(OPh)_2$, $Tp^*WS(SPh)_2$, Tp*WS(tdt), Tp*WS(qdt), and $Tp^*WS(SePh)_2$ from ZORA-B3LYP DFT calculations.

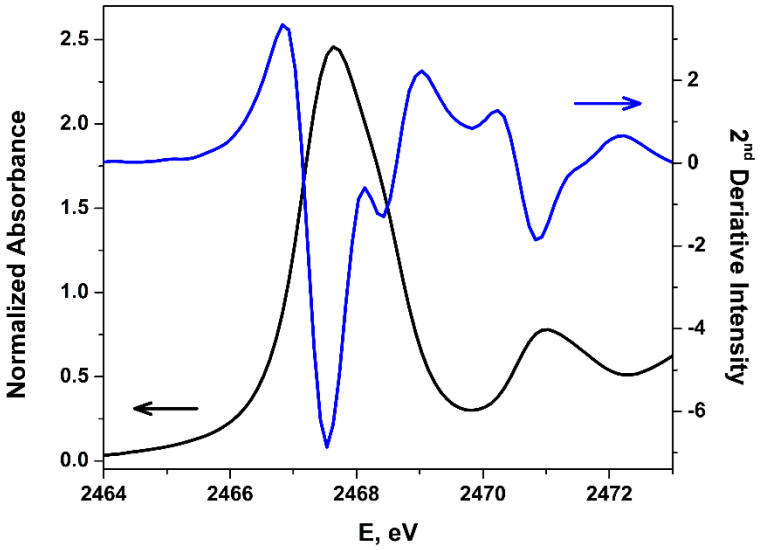

Figure S6. Overlay of the normalized S K-edge spectrum (black) for Tp*$WSCl_2$ and its second derivative (blue).

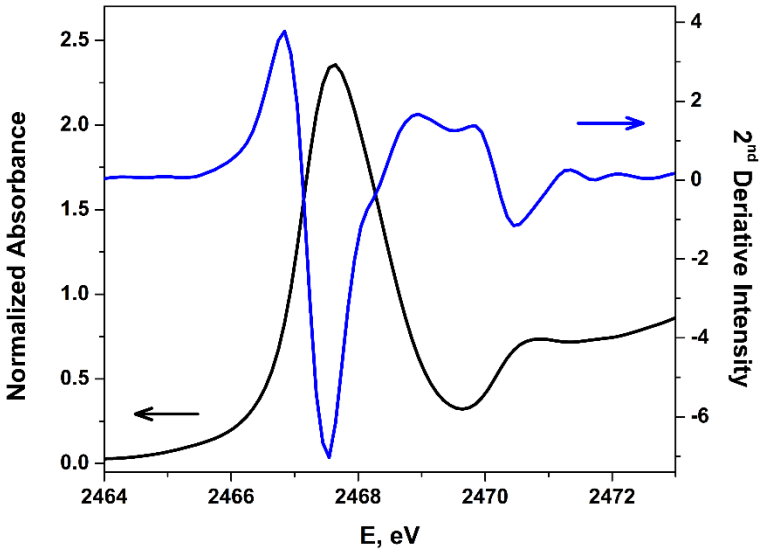

Figure S7. Overlay of the normalized S K-edge spectrum (black) for Tp*$WS(OPh)_2$ and its second derivative (blue).

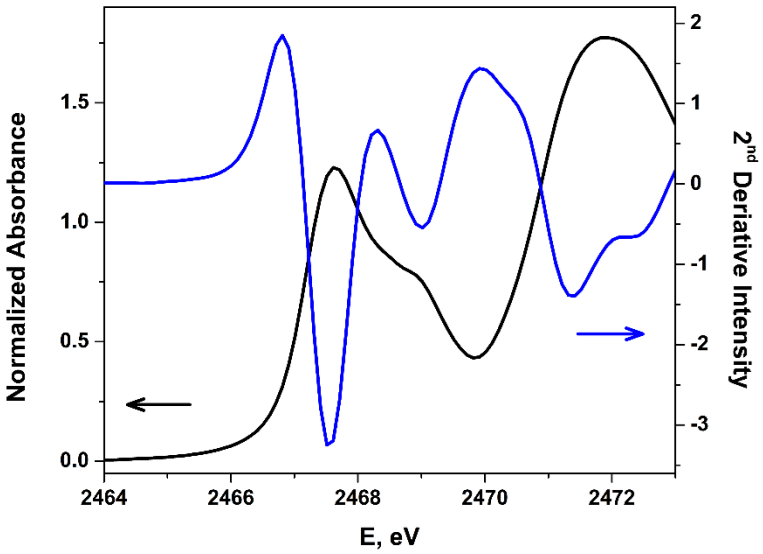

Figure S8. Overlay of the normalized S K-edge spectrum (black) for Tp*WS(SPh)$_2$ and its second derivative (blue).

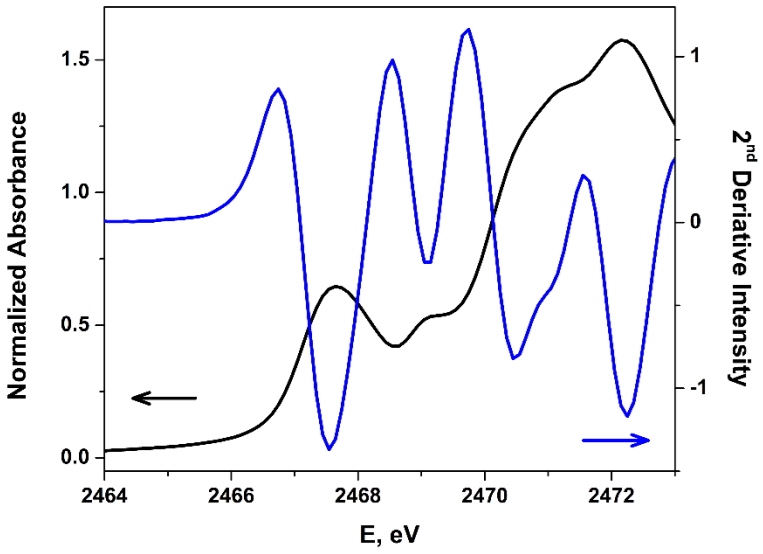

Figure S9. Overlay of the normalized S K-edge spectrum (black) for Tp*WS(tdt) and its second derivative (blue).

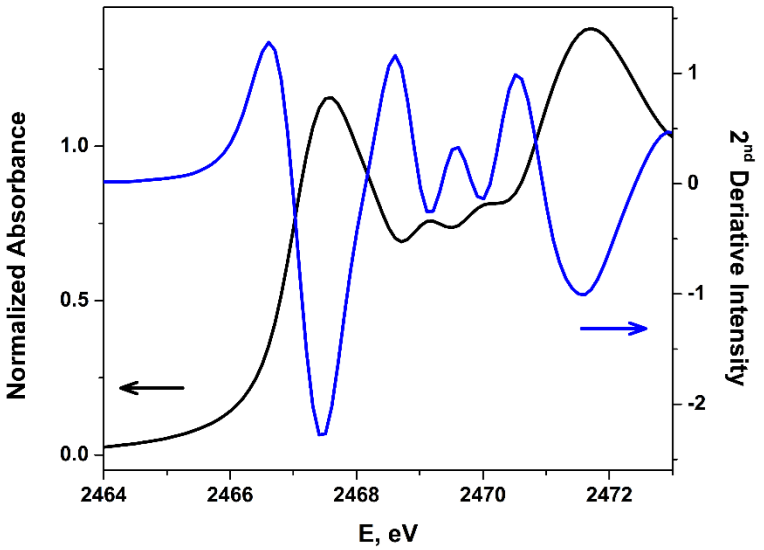

Figure S10. Overlay of the normalized S K-edge spectrum (black) for Tp*WS(qdt) and its second derivative (blue).

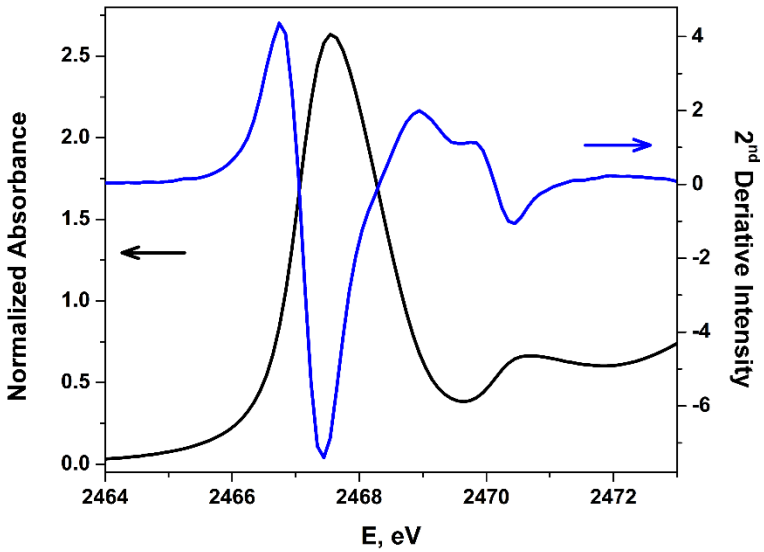

Figure S11. Overlay of the normalized S K-edge spectrum (black) for Tp*WS(SePh)$_2$ and its second derivative (blue).

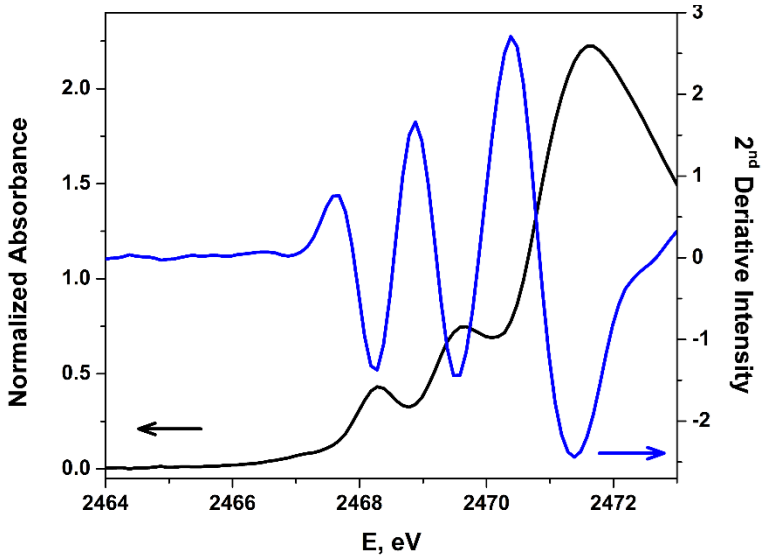

Figure S12. Overlay of the normalized S K-edge spectrum (black) for Tp*WO(SPh)$_2$ and its second derivative (blue).

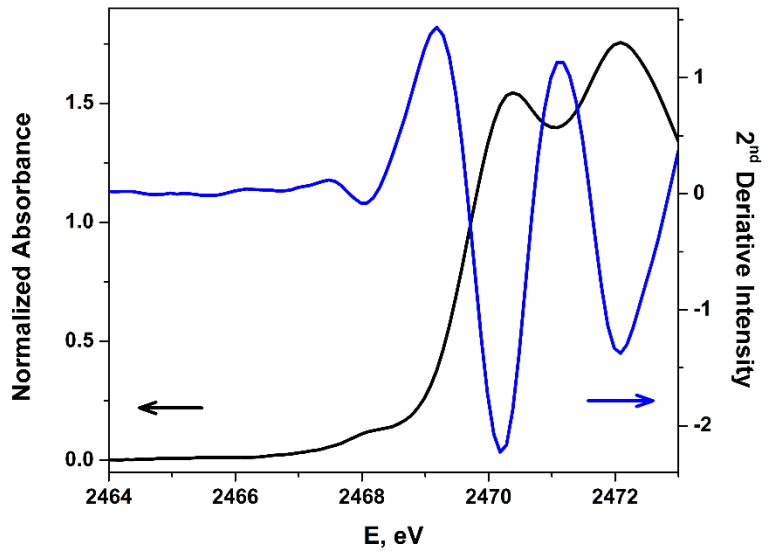

Figure S13. Overlay of the normalized S K-edge spectrum (black) for Tp*WS(tdt) and its second derivative (blue).

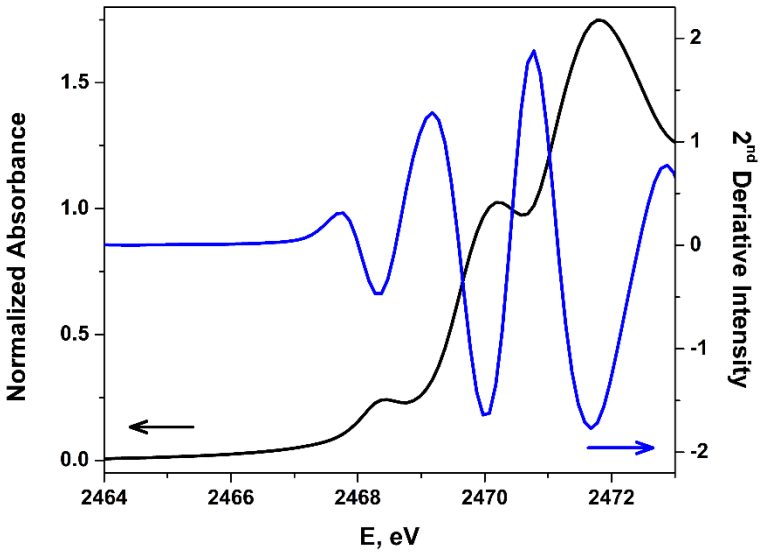

Figure S14. Overlay of the normalized S K-edge spectrum (black) for Tp*WO(qdt) and its second derivative (blue).

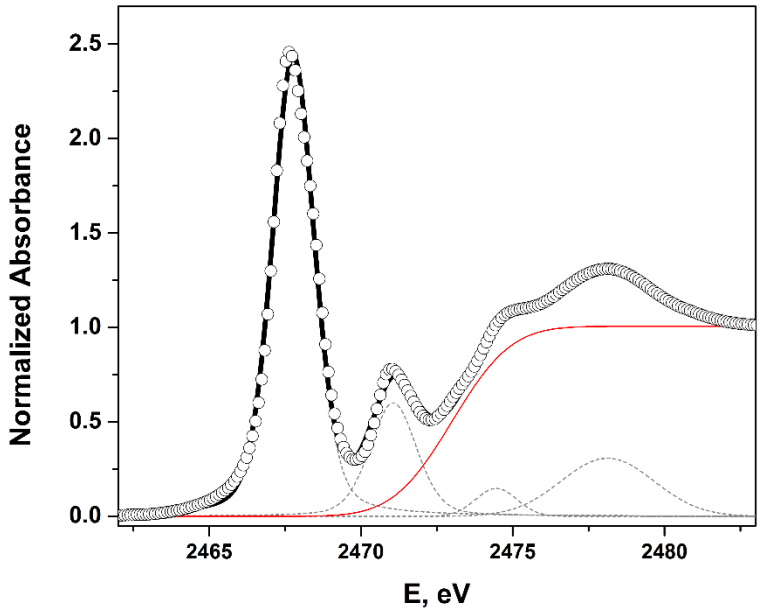

Figure S15. Pseudo-Voigt deconvolution of the S K-edge spectrum of Tp*$WSCl_2$. Circles represent the experimental data; dashed lines the pseudo-Voigt peaks; the red trace is the rising-edge; and the solid line the sum of the fit).

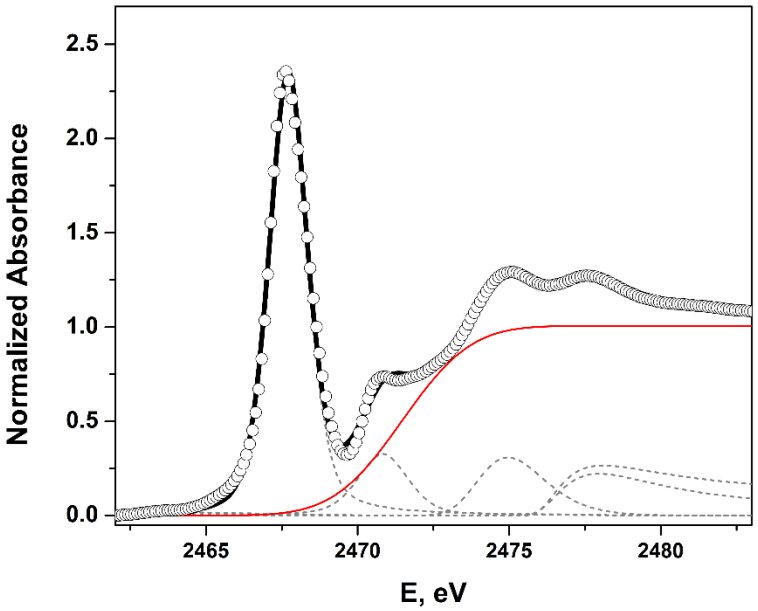

Figure S16. Pseudo-Voigt deconvolution of the S K-edge spectrum of Tp*WS(OPh)$_2$. Circles represent the experimental data; dashed lines the pseudo-Voigt peaks; the red trace is the rising-edge; and the solid line the sum of the fit).

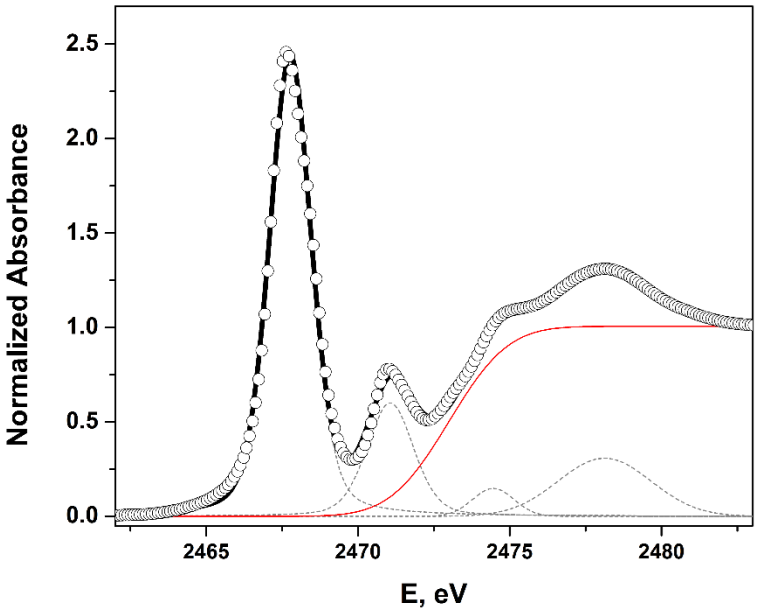

Figure S17. Pseudo-Voigt deconvolution of the S K-edge spectrum of Tp*WS(SPh)$_2$. Circles represent the experimental data; dashed lines the pseudo-Voigt peaks; the red trace is the rising-edge; and the solid line the sum of the fit).

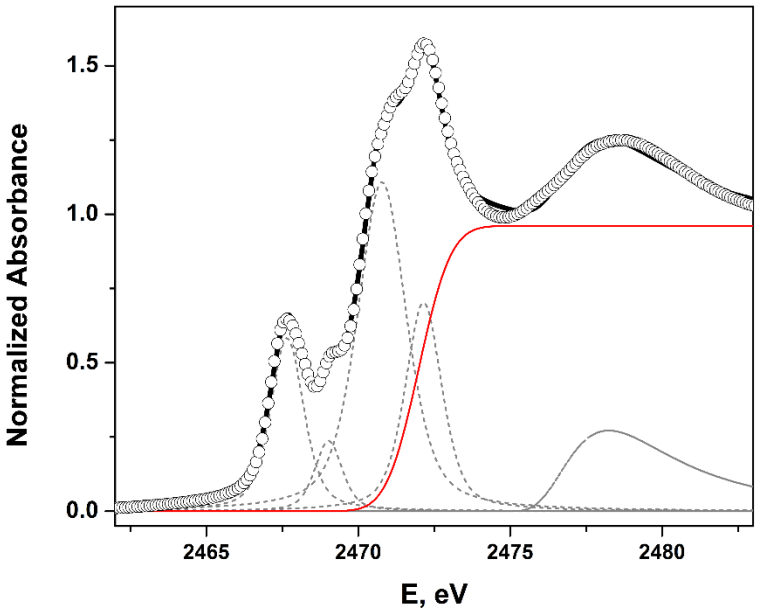

Figure S18. Pseudo-Voigt deconvolution of the S K-edge spectrum of Tp*WS(tdt). Circles represent the experimental data; dashed lines the pseudo-Voigt peaks; the red trace is the rising-edge; and the solid line the sum of the fit).

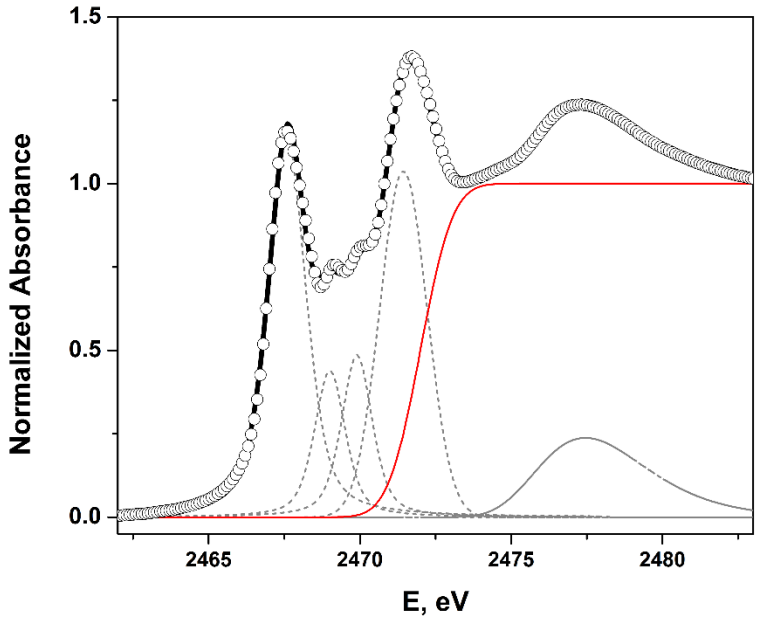

Figure S19. Pseudo-Voigt deconvolution of the S K-edge spectrum of Tp*WS(qdt). Circles represent the experimental data; dashed lines the pseudo-Voigt peaks; the red trace is the rising-edge; and the solid line the sum of the fit).

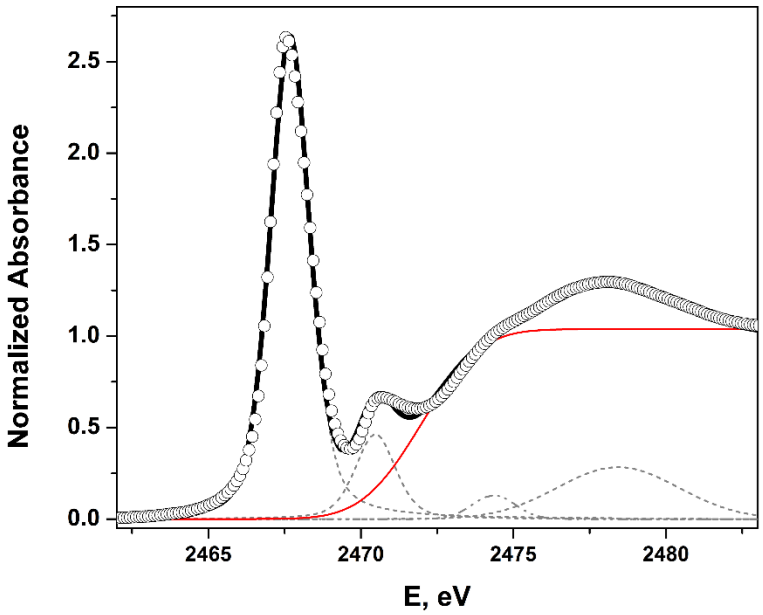

Figure S20. Pseudo-Voigt deconvolution of the S K-edge spectrum of Tp*WS(SePh)$_2$. Circles represent the experimental data; dashed lines the pseudo-Voigt peaks; the red trace is the rising-edge; and the solid line the sum of the fit).

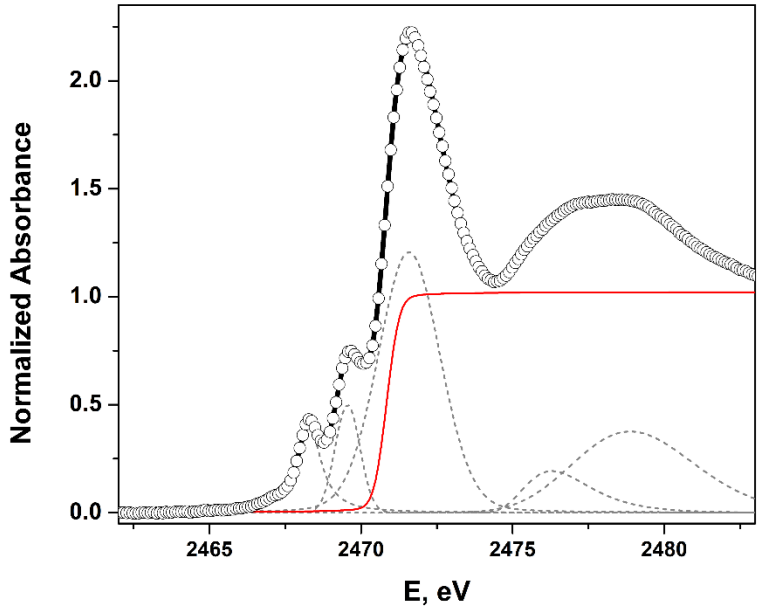

Figure S21. Pseudo-Voigt deconvolution of the S K-edge spectrum of Tp*WO(SPh)$_2$. Circles represent the experimental data; dashed lines the pseudo-Voigt peaks; the red trace is the rising-edge; and the solid line the sum of the fit).

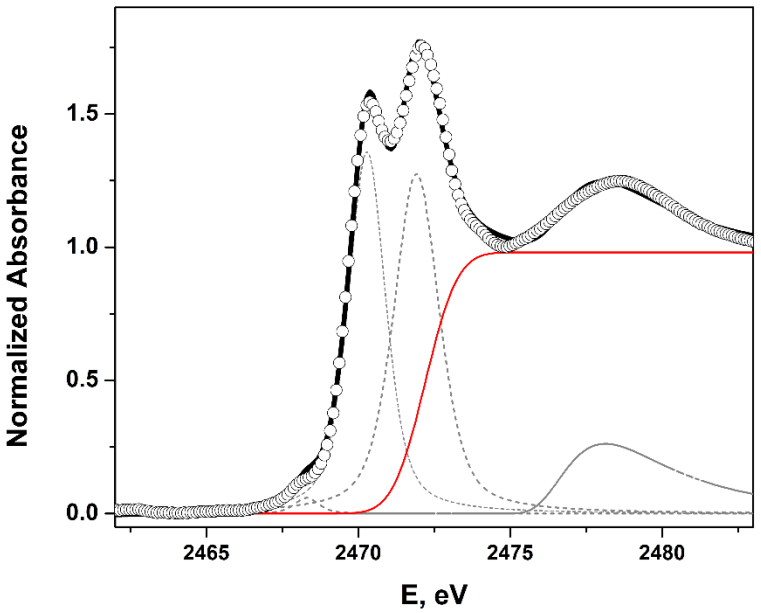

Figure S22. Pseudo-Voigt deconvolution of the S K-edge spectrum of Tp*WO(tdt). Circles represent the experimental data; dashed lines the pseudo-Voigt peaks; the red trace is the rising-edge; and the solid line the sum of the fit).

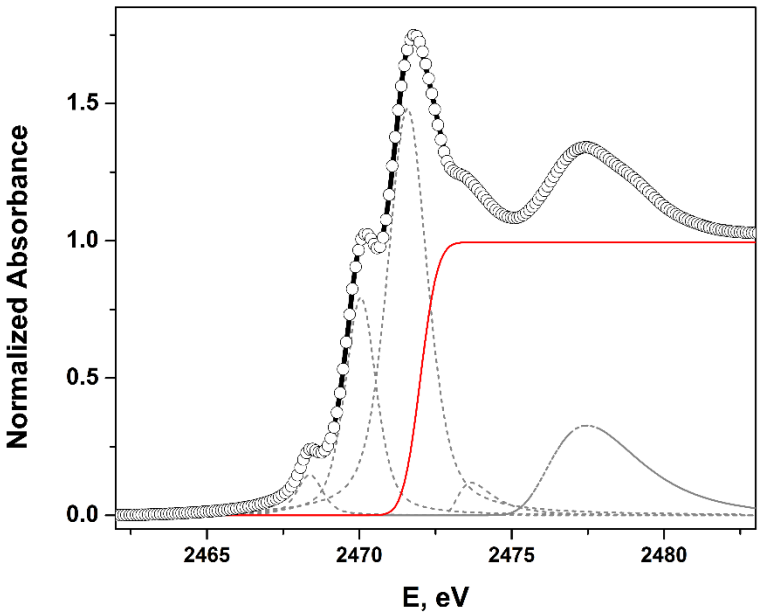

Figure S23. Pseudo-Voigt deconvolution of the S K-edge spectrum of Tp*WO(qdt). Circles represent the experimental data; dashed lines the pseudo-Voigt peaks; the red trace is the rising-edge; and the solid line the sum of the fit).

Table S1. Geometry Optimized Coordinates for Tp*$WSCl_2$

W	0.000000000	0.000000000	0.000000000
Cl	1.604290000	-1.676800000	-0.441670000
Cl	1.610900000	1.676800000	-0.434000000
S	0.000000000	0.000000000	2.150600000
N	-1.574510000	1.491300000	-0.154470000
N	-2.685770000	1.265960000	-0.936700000
N	-1.579920000	-1.484330000	-0.171360000
N	-2.685260000	-1.254750000	-0.961280000
N	-0.319840000	0.002070000	-2.344780000
N	-1.604960000	0.025830000	-2.826010000
C	-3.559780000	2.293520000	-0.803810000
C	-3.004860000	3.203790000	0.090610000
C	-1.766570000	2.679310000	0.481440000
C	-3.561530000	-2.281580000	-0.839120000
C	-3.015150000	-3.195150000	0.057590000
C	-1.777530000	-2.675950000	0.456540000
C	-1.605480000	0.046520000	-4.182430000
C	-0.277920000	0.033240000	-4.591590001
C	0.501750000	0.004280000	-3.423650000
B	-2.773810000	0.014060000	-1.834400000
H	-4.507271251	2.285413769	-1.362553870
H	-3.551055767	4.122689956	0.350019244
H	-1.000289675	3.064694836	1.170129346
H	-4.541636433	-2.479746698	-1.297509923
H	-3.566201157	-4.112392605	0.312557954
H	-1.015066745	-3.067414041	1.146036690
H	-2.558215768	0.068904290	-4.731787329
H	-0.032710368	0.045763475	-5.663837779
H	1.592705989	-0.015061015	-3.284219666
H	-3.727141900	0.019218144	-2.383154624

Table S2. Geometry Optimized Coordinates for Tp*WS(SPh)$_2$

W	0.006384	0.014833	0.034881
S	1.666935	-1.666832	-0.317971
S	1.529055	1.780550	-0.513348
S	0.079946	0.055393	2.198302
N	-0.365857	-0.226276	-2.284906
N	-1.661262	-0.324134	-2.723467
N	-1.708982	1.364319	-0.116795
N	-2.781001	1.065043	-0.939587
N	-1.533065	-1.593352	0.014432
N	-2.682091	-1.439293	-0.729729
C	0.424642	-0.298041	-3.381736
C	-0.382892	-0.445829	-4.518273
C	-1.695831	-0.462464	-4.074869
C	-2.957443	-0.617758	-4.864907
C	-2.022067	2.514760	0.545489
C	-3.291599	2.947857	0.128813
C	-3.743104	2.013357	-0.804718
C	-1.160093	3.144810	1.577027
C	-5.037330	1.993941	-1.547442
C	-1.679068	-2.737623	0.735708
C	-2.926222	-3.305583	0.438964
C	-3.535282	-2.465400	-0.488138
C	-0.674018	-3.265728	1.698224
C	-4.876531	-2.602119	-1.135752
C	3.056909	-1.638186	0.788421
C	3.793634	-2.833762	0.897916
C	4.870085	-2.921815	1.777239
C	5.239939	-1.816963	2.552498
C	4.522134	-0.624249	2.432911
C	3.437043	-0.528991	1.560904
C	0.868133	3.244401	-1.304973
C	1.464064	4.472590	-0.970343
C	1.039275	5.654629	-1.577297
C	0.018053	5.632384	-2.531273
C	-0.564308	4.411653	-2.879292
C	-0.143228	3.225137	-2.278933
B	-2.822062	-0.262292	-1.710693
H	-3.864838	-0.344462	-2.295059
H	3.501685	-3.695846	0.298656
H	5.418983	-3.859204	1.863315
H	6.079859	-1.886991	3.242537
H	4.805637	0.245568	3.025471
H	2.887620	0.405714	1.472666
H	2.261370	4.492585	-0.228034
H	1.508811	6.598681	-1.300808
H	-0.316747	6.556546	-3.001908
H	-1.354885	4.376175	-3.628281
H	-0.596529	2.280720	-2.567977
H	-0.043208	-0.531516	-5.547279
H	-3.809650	3.833826	0.460861
H	-3.332646	-4.220393	0.852839
H	-2.708446	-0.721115	-5.927093

H	-3.626124	0.245660	-4.754394
H	-3.519837	-1.510482	-4.561947
H	-1.561628	4.128985	1.845444
H	-0.125690	3.262847	1.229700
H	-1.122787	2.519633	2.483108
H	-5.618465	2.887223	-1.292010
H	-5.642601	1.112945	-1.292002
H	-4.887864	1.984578	-2.635490
H	-1.004135	-4.239375	2.077850
H	-0.543141	-2.579908	2.547291
H	0.310683	-3.375893	1.224901
H	-5.365084	-3.512849	-0.772354
H	-4.801419	-2.669435	-2.228894
H	-5.530469	-1.751422	-0.901504
C	1.918770	-0.221078	-3.376705
H	2.270478	0.610217	-2.753165
H	2.360977	-1.138313	-2.967872
H	2.277912	-0.080876	-4.401788

Table S3. Geometry Optimized Coordinates for Tp*WS(qdt)

W	-0.000967	-0.019507	0.043258
S	1.693022	1.581115	-0.424185
S	1.688697	-1.630006	-0.393481
S	0.050785	-0.009409	2.200746
C	3.171793	0.704709	0.003569
C	3.161825	-0.749529	0.046030
N	-0.406630	-0.033986	-2.320219
N	-1.617459	-1.507898	-0.084512
N	-2.748310	-1.268748	-0.832199
N	-2.730108	1.254184	-0.852468
N	-1.601997	1.483965	-0.100478
N	-1.711330	-0.032481	-2.750488
N	4.264494	1.386992	0.245461
N	4.237639	-1.430066	0.365461
C	-3.648126	-2.261095	-0.639668
C	-1.795899	2.658633	0.562135
C	-3.054355	3.164739	0.223230
C	-4.988732	-2.306148	-1.303598
C	-3.089635	-3.169415	0.254441
C	-0.841680	-3.282737	1.528345
C	0.365650	-0.048632	-3.436756
B	-2.847148	-0.013574	-1.725071
C	-3.622709	2.259620	-0.670078
C	1.857385	-0.054251	-3.464900
C	-1.770274	-0.047192	-4.106187
C	-0.462399	-0.057343	-4.570407
C	5.390530	0.696529	0.589513
C	5.371829	-0.733922	0.667489
C	-1.820132	-2.675072	0.583581
C	-0.815735	3.258283	1.511374
C	-4.957759	2.317279	-1.337453
C	6.584486	1.392458	0.896453

C	-3.045409	-0.050448	-4.887916
C	6.539532	-1.423235	1.070200
C	7.711146	0.694068	1.282610
C	7.688600	-0.717671	1.375569
H	-3.502641	4.081683	0.589213
H	-4.902244	-2.323077	-2.397525
H	-5.605735	-1.438719	-1.035217
H	-5.520587	-3.210585	-0.990103
H	-3.543345	-4.080286	0.625452
H	-0.658178	-2.615217	2.382666
H	0.131083	-3.459220	1.050846
H	-1.234006	-4.234870	1.901692
H	-3.905978	-0.012746	-2.284664
H	2.271050	0.817135	-2.941541
H	2.198947	-0.033327	-4.506144
H	2.264427	-0.950782	-2.979871
H	-0.137887	-0.071089	-5.604732
H	-0.640471	2.589335	2.366230
H	-1.203590	4.212807	1.884145
H	0.160112	3.428991	1.038549
H	-5.577249	1.445670	-1.088724
H	-4.867562	2.355987	-2.430958
H	-5.490574	3.216627	-1.008877
H	6.577257	2.479590	0.828455
H	-3.674896	-0.916362	-4.644491
H	-2.814842	-0.091682	-5.958166
H	-3.641860	0.853404	-4.705593
H	6.498499	-2.509271	1.134212
H	8.626700	1.232788	1.525283
H	8.584387	-1.249903	1.691791

Table S4. Geometry Optimized Coordinates for Tp*WO(tdt)

W	0.041949	0.001505	-0.018921
S	1.722696	-1.613232	-0.483746
S	1.741624	1.608640	-0.472987
O	0.086205	-0.010546	1.699489
N	-1.571300	1.507010	-0.117869
N	-2.696975	1.309060	-0.882478
N	-1.610373	-1.430008	-0.109069
N	-2.732403	-1.215846	-0.874619
N	-0.410478	0.007519	-2.391155
N	-1.720544	0.031553	-2.807898
C	3.215927	-0.719744	-0.137264
C	3.225981	0.696660	-0.140276
C	4.435587	1.378398	0.053007
C	5.641852	0.695040	0.238493
C	5.613763	-0.709227	0.248576
C	4.420608	-1.405353	0.067887
C	-3.577247	2.319381	-0.671593
C	-3.011372	3.183002	0.262430
C	-1.758756	2.647311	0.593371
C	-0.762096	3.197730	1.561562

C	-4.902631	2.420721	-1.357391
C	-3.647930	-2.184707	-0.622811
C	-3.106078	-3.038228	0.337241
C	-1.834771	-2.537561	0.644155
C	-0.857336	-3.056303	1.645284
C	-4.974037	-2.269907	-1.309093
C	-1.793761	0.053712	-4.162423
C	-0.490922	0.039086	-4.641060
C	0.348479	0.009961	-3.515132
C	1.839290	-0.015959	-3.543868
C	-3.078869	0.095695	-4.926825
B	-2.838223	0.045585	-1.765601
H	-3.907724	0.061052	-2.304267
H	4.425454	2.469461	0.044038
H	6.541370	-1.264798	0.393834
H	4.415287	-2.494380	0.073457
H	-3.455376	4.088912	0.659002
H	-1.286414	3.723761	2.369098
H	-0.091368	3.917352	1.070246
H	-0.144545	2.405898	1.997050
H	-5.556225	1.572913	-1.112318
H	-4.793588	2.448689	-2.449326
H	-5.407548	3.340662	-1.042123
H	-3.577691	-3.915441	0.765104
H	-1.249501	-3.967599	2.110245
H	-0.668263	-2.308035	2.426638
H	0.113159	-3.278753	1.181667
H	-5.500397	-1.307934	-1.306011
H	-5.603239	-3.009205	-0.801482
H	-4.864233	-2.582473	-2.357284
H	-0.177798	0.048537	-5.679002
H	2.185889	0.010740	-4.583393
H	2.229903	-0.921748	-3.061817
H	2.262154	0.841961	-3.005217
H	-3.722136	-0.764314	-4.698426
H	-2.863467	0.082683	-6.000969
H	-3.654595	1.005718	-4.709526
C	6.936943	1.454991	0.405061
H	6.900451	2.126196	1.274804
H	7.147010	2.079160	-0.475669
H	7.784633	0.772623	0.540830

Table S5. Geometry Optimized Coordinates for Tp*WO(qdt)

W	0.003955	-0.017482	0.019099
S	1.716096	1.593129	-0.406792
S	1.712311	-1.636799	-0.378244
O	-0.017521	-0.014547	1.738175
C	3.186992	0.704996	0.029789
C	3.176245	-0.745655	0.077303
N	-0.418491	-0.032189	-2.356236
N	-1.621609	-1.484494	-0.107456
N	-2.751556	-1.263499	-0.858395

N	-2.730709	1.255967	-0.874422
N	-1.599993	1.467038	-0.121282
N	-1.724890	-0.031478	-2.785699
N	4.284799	1.387120	0.272258
N	4.251680	-1.426173	0.407843
C	-3.659479	-2.240780	-0.617005
C	-1.801198	2.591148	0.612699
C	-3.069521	3.102009	0.309081
C	-5.003115	-2.302328	-1.269940
C	-3.103588	-3.110433	0.318851
C	-0.839310	-3.159728	1.592096
C	0.350857	-0.054596	-3.473245
B	-2.856133	-0.008689	-1.757209
C	-3.631117	2.240277	-0.630194
C	1.842879	-0.056542	-3.490306
C	-1.785568	-0.058599	-4.140537
C	-0.477986	-0.072816	-4.606803
C	5.409311	0.697722	0.611281
C	5.387091	-0.733274	0.699838
C	-1.831284	-2.609619	0.622764
C	-0.806925	3.128450	1.587189
C	-4.972091	2.318830	-1.286378
C	6.609503	1.391668	0.902232
C	-3.061928	-0.068243	-4.920666
C	6.558699	-1.421310	1.101201
C	7.737074	0.694764	1.283627
C	7.709817	-0.718250	1.389944
H	-3.524060	3.993910	0.724922
H	-4.924759	-2.345234	-2.363748
H	-5.619648	-1.429662	-1.016881
H	-5.532060	-3.199794	-0.931420
H	-3.564977	-4.000238	0.731499
H	-0.569114	-2.407784	2.345091
H	0.091456	-3.457681	1.090620
H	-1.262918	-4.034820	2.097022
H	-3.920155	-0.001570	-2.307967
H	2.247785	0.809302	-2.950748
H	2.195934	-0.021662	-4.527198
H	2.246866	-0.957434	-3.010020
H	-0.155374	-0.095025	-5.641253
H	-0.540282	2.368130	2.333140
H	-1.226626	4.000443	2.100715
H	0.125246	3.427248	1.088831
H	-5.583088	1.431838	-1.074508
H	-4.887784	2.409097	-2.377062
H	-5.508886	3.197866	-0.913114
H	6.604781	2.478206	0.821901
H	-3.702776	-0.917665	-4.650491
H	-2.833538	-0.144021	-5.989493
H	-3.645766	0.849090	-4.765503
H	6.514710	-2.507884	1.174318
H	8.657235	1.231090	1.511678
H	8.608108	-1.248519	1.703362

Table S6. Geometry Optimized Bond Distances (Å) and Angles (°) for Complexes[a]

Distance/Angle	Tp*$WSCl_2$	Tp*$WS(SPh)_2$
W–S1	2.151	2.165
W–X2	2.362	2.390
W–X3	2.365	2.395
W–N11	2.366	2.362
W–N21	2.175	2.226
W–N31	2.174	2.188
S1–W–X2	100.78	97.88
S1–W–X3	100.57	101.15
X2–W–X3	90.7	92.48
W–X2–C41		116.13
W–X3–C51		117.98

[a] X refers to the donor atom of the monodentate coligand.

Table S7. Geometry Optimized Bond Distances (Å) and Angles (°) for Complexes

Distance/Angle	Tp*WS(qdt)	Tp*WO(tdt)	Tp*WO(qdt)
W–E1[a]	2.158	1.719	1.719
W–S2	2.375	2.377	2.387
W–S3	2.377	2.383	2.389
W–N11	2.398	2.415	2.413
W–N21	2.201	2.188	2.193
W–N31	2.201	2.209	2.190
E1–W–S2	99.79	99.94	100.17
E1–W–S3	100.16	100.19	100.72
S2–W–S3	85.03	85.21	85.11
W–S2–C41	102.06	102.41	101.95
W–S3–C51	102.37	102.38	102.30
fold angle[b]	31.3	28.1	30.4

[a] E refers to the terminal chalcogenide ligand, O or S. [b] Dihedral angle between the WS_2 and S_2C_2 planes.

Table S8. Contributions (%) to the Lowest Unoccupied MOs Derived from B3LYP DFT Calculations[a]

Complex	$d_{x^2-y^2}$[b]			$d_{xz,yz}$[c]			d_{z^2}			d_{xy}		
	W 5d	S_a 3p	S_e 3p	W 5d	S_a 3p	S_e 3p	W 5d	S_a 3p	S_e 3p	W 5d	S_a 3p	S_e 3p
Tp*WSCl_2	66.2	0.1		51.9	22.9		39.7	11.5		53.7	0.0	
Tp*WS$(OPh)_2$	63.6	1.3		45.4	19.0		35.3	9.8		45.5	2.4	
Tp*WS$(SPh)_2$	55.1	4.3	9.7	47.5	20.5	5.7	23.0	4.5	6.7	39.3	2.3	10.7
Tp*WS(tdt)	62.8	2.7	4.2	47.7	20.6	6.6	33.6	10.5	7.5	34.8	0.1	14.6
Tp*WS(qdt)	60.7	2.2	3.5	46.5	20.1	4.3	33.8	10.4	7.9	35.9	0.1	15.0
Tp*WS$(SePh)_2$	56.7	3.2		46.9	20.9		20.8	4.7		38.8	0.9	
Tp*WO$(SPh)_2$	54.6		12.9	47.2		4.2				39.2		11.0
Tp*WO(tdt)	61.7		5.5	45.0		4.5				30.5		13.4
Tp*WO(qdt)	61.2		4.1	46.8		6.7				36.7		15.1

[a] S_a = apical sulfide ligand; S_e = equatorial sulfur-donor coligand. [b] β-spin (spin down) orbital only. [c] Averaged value for the near degenerate orbitals.

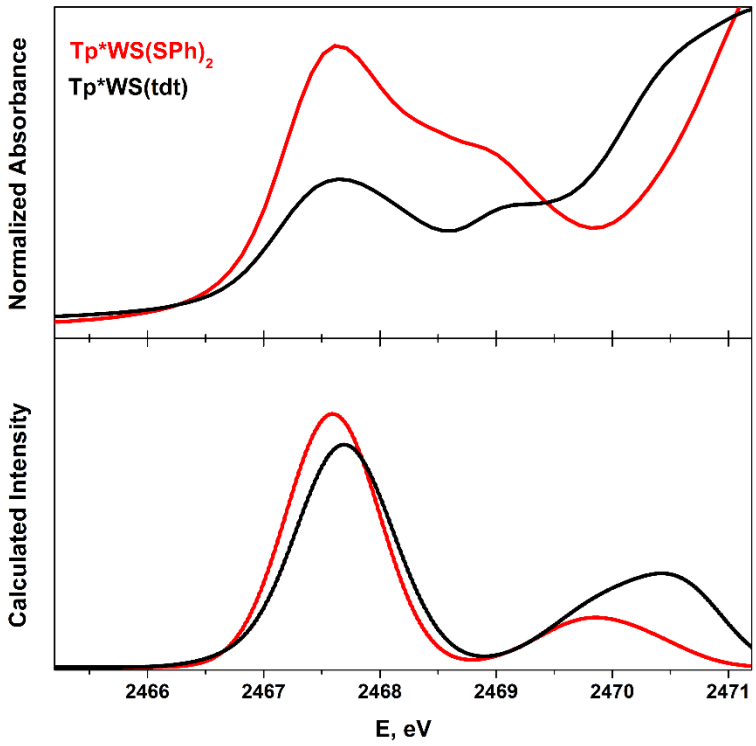

Figure S24. Comparison of the experimental (top) and calculated (bottom) S K-pre-edge spectra for Tp*WS(SPh)2 and Tp*WS(tdt) obtained from ZORA-BP86 TD-DFT calculations. Calculated intensity in arbitrary units.

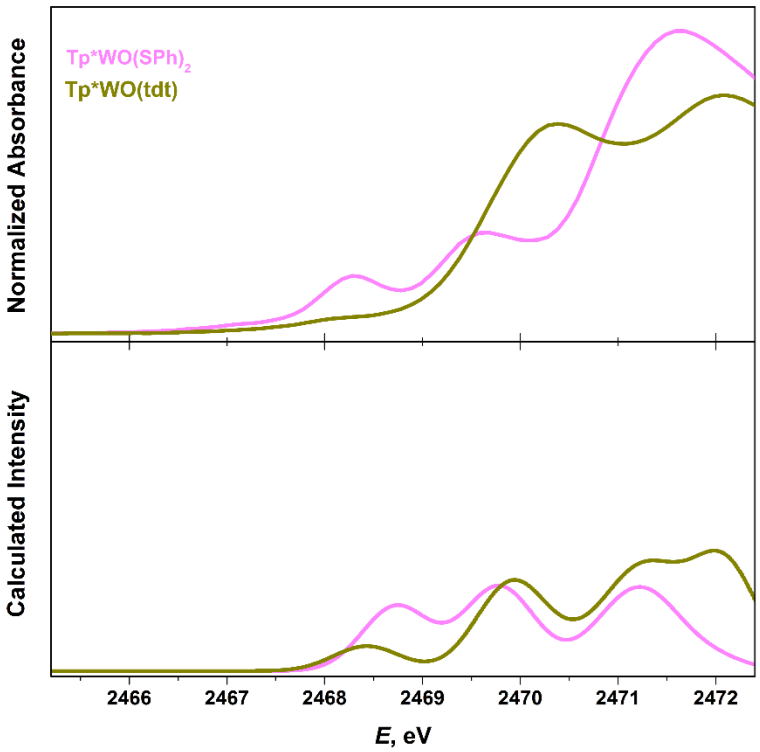

Figure S25. Comparison of the experimental (top) and calculated (bottom) S K-pre-edge spectra for Tp*WO(SPh)2 and Tp*WO(tdt) obtained from ZORA-BP86 TD-DFT calculations. Calculated intensity in arbitrary units.